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Synthesis and crystal structure of complexes of bipodal thiophosphorylated thioureas with divalent transition metals

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Abstract

New complexes of bipodal thiophosphorylated thioureas $\{[(i\mathrm{PrO})_2\mathrm{P(S)NC(S)NH}]_2\mathrm{Z}\}\mathrm{M}$, where Z = *m*-$C_6H_4$, *p*-$C_6H_4$, M = Co, Ni, Zn, Cd have been prepared and characterized. The crystal and molecular structures of Cd(II), Z = CH_2CH_2 and Pd(II), Z = $(CH_2CH_2)_2O$ complexes have been determined by single crystal X-ray diffraction analyses. Both complexes are binuclear in the solid state with a M_2L_2 stoichiometry. The cadmium and palladium atoms are four-coordinated and have the configuration of a slightly distorted tetrahedron for cadmium and a distorted square plane for palladium. Metal-containing macrocycles are formed as well as two spirocycles.

Keywords: *P*,*S*-metallocycles; Supramolecular chemistry; Bipodal ligands; Crystal structures; Macrocycles; Phosphorylated urea complexes

1. Introduction

We have recently reported the syntheses and complexing properties of bipodal thiophosphorylated thioureas $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NH}]_2\mathrm{Z}$, where Z = $(CH_2)_2$, $(CH_2)_7$, $(CH_2)_2O(CH_2)_2$, $(CH_2)_2O(CH_2)_2O(CH_2)_2$, and some properties of the chelate complexes formed by these ligands with a series of metal ions [1,2].

In this paper, we report on the synthesis of the bis-urea $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NH}]_2\mathrm{Z}$ complexes with Co(II), Ni(II), Zn(II) and Cd(II) (Z = *m*-C_6H_4, *p*-C_6H_4), together with the X-ray study of the bis-urea $[(i\mathrm{PrO})_2\mathrm{P(S)NHC(S)NHCH_2}]_2$ and the complexes with the cadmium(II) ion (**1**) (Z = CH_2CH_2) and the palladium(II) ion (**2**) (Z = $(CH_2CH_2)_2O$).

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2. Experimental

2.1. Synthesis of $[(iPrO)_2P(S)NHC(S)NH]_2$-*m*-C_6H_4 (**3**)

A solution of *m*-phenylenediamine (2.163 g, 0.02 mol) in anhydrous benzene (50 ml) was added dropwise under stirring to a benzene solution (25 ml) of diisopropylthiophosphoryl isothiocyanate (9.572 g, 0.04 mol). The mixture was heated to 60 °C and stirred for 2 h. The solvent was removed in vacuum. A colourless precipitate was crystallized from benzene. Yield: 8.33 g (~71%), m.p. 122 °C. *Anal.* Calc. for $C_{20}H_{36}N_4O_4P_2S_4$: C, 40.95; H, 6.14; P, 10.58. Found: C, 41.58; H, 6.25; P, 10.30%. ^{1}H NMR (C_6D_6) 1.33 (d, 24H, CH_3, $^3J_{HH}$ 6.1 Hz), 4.78 (d, sept, 4H, OCH, $^3J_{HH}$ 6.3 Hz, $^3J_{POCH}$ 10.7 Hz), 6.86 (d, 2H, NHP(S), $^2J_{PH}$ 9.8 Hz), 7.24 (t, 1H, *m*-C_6H_4, $^3J_{HH}$ 8.2 Hz), 7.46 (d. d, 2H, *m*-C_6H_4, $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.9 Hz), 8.14 (m, 1H, *m*-C_6H_4), 9.68 (s, 2H, C_6H_4NH). ^{31}P{^{1}H} NMR (ppm), 53.5. IR (cm^{-1}):